

METHOD OF DETERMINING THE IMPEDANCE OF AN ELECTROCHEMICAL SYSTEM

To determine properties and qualities of an electrochemical system (such as a cell, a battery, an electrodeposition system, a system for analyzing a medium) and predict its future operation, one of the basic parameters is the system's
5 impedance.

Generally, an electrochemical system comprises, in an electrolytic medium, two main electrodes - a work electrode and a back-electrode. A reference electrode is arranged in the vicinity of the work electrode and is used in relation therewith
10 to perform various measurement or regulation operations. In the following, the mentioned voltages and currents correspond to measurements performed between a work electrode and the corresponding reference electrode.

The impedance of an electrochemical system corresponds
15 to the voltage/current ratio. It is known that to rapidly measure the value of this impedance according to frequency, it is desirable to calculate the ratio of the discrete Fourier transforms (DFT) of the voltage and of the current. For this purpose, an excitation signal of small amplitude is applied
20 between a reference electrode and a work electrode of an electrochemical cell, and N successive values $e(n)$ and $i(n)$ of the voltage and of the current, with $1 \leq n \leq N$, are measured at

equal time intervals ΔT . The general expression of discrete Fourier transforms $E(f_m)$ and $I(f_m)$ of the voltage and of the current for a sequence of N points is:

$$E(f_m) = \Delta T \sum_{n=1}^N e(n) \exp(-2\pi j f_m n \Delta T) \quad (1)$$

$$I(f_m) = \Delta T \sum_{n=1}^N i(n) \exp(-2\pi j f_m n \Delta T) \quad (2)$$

where j designates the complex number having -1 as a square, N designates the number of measurement points, ΔT the sampling interval. The calculation of the discrete Fourier transform may be performed for $N/2$ values of frequency f_m , with $0 \leq m < (N/2) - 1$, N being an even number. These $N/2$ discrete frequencies are regularly distributed between 0 and $1/2\Delta T$ ($0 \dots 1/m\Delta T \dots 1/2\Delta T$).

The complex impedance for a given frequency f_m is then equal to:

$$Z(f_m) = E(f_m) / I(f_m). \quad (3)$$

The impedance measurement methods used in practice, mainly differ by the type of excitation signal of the system: sinusoidal, multi-sinusoidal, white noise, etc. A sinusoidal excitation is by far the most widely used, since it appears to be the most accurate. The method consists of imposing a sinusoidal regulation to the electrochemical cell with a signal of small amplitude and of recording the cell current and voltage response. The ratio of the Fourier transforms of the voltage and of the current at the sinus frequency will give the impedance value at this frequency. The frequency spectrum is swept by modifying the excitation frequency.

In the theory of electric systems, the expression of the impedance (equation (3)) is correct, provided that the analyzed system is linear and stationary and that disturbances are not introduced by phenomena external to the system. In the case of electrochemical systems, the fulfilling of these conditions imposes specific precautions. The transfer function of an electrochemical system is generally non-linear but it can be considered as linear over a small portion. This is why a low-

amplitude excitation signal is used. Accordingly, the signal-to-noise ratio decreases and the measurement time, that is, the number of measurement points, must be increased to suppress the noise by an integration of the response. However, the lengthening of the measurement time sets problems regarding to the stationarity of the electrochemical system. In many real cases, the stationarity condition cannot be fulfilled. The causes are many: voltage relaxation, current relaxation, concentration relaxation. In such conditions, if the measurement time is sufficiently long to have a good signal-to-noise ratio, the system is not stationary during the measurement time and the calculated impedance has no great meaning any more, especially at low frequencies (for example, smaller than one hertz) where non-stationarity problems are particularly serious.

Various methods have been provided to solve this problem of the non-stationarity of electrochemical systems, but none has yielded a satisfactory solution.

Thus, an object of the present invention is to provide a novel method for calculating the impedance of an electrochemical system enabling ignoring errors linked to the system non-stationarity.

To achieve this object, the present invention provides a method for determining the complex impedance $Z(f_m)$ of a non-stationary electrochemical system, comprising the steps of:

setting the system to a selected voltage state and applying a sinusoidal signal of frequency f_m thereto,

measuring, immediately after, successive values of the voltage and of the current at regular time intervals ΔT ,

calculating the discrete Fourier transforms of the voltage ($E(f)$) and of the current ($I(f)$), the voltage transform being calculated for the sole frequency f_m of the sinusoidal signal and the current transform being calculated for frequency f_m and for two adjacent frequencies f_{m-1} and f_{m+1} on either side of frequency f_m , and

calculating the impedance according to the following formula:

$$Z(f_m) = E(f_m) / I^*(f_m)$$

where I^* designates a corrected current such that:

$$\begin{aligned} \text{Re}[I^*(f_m)] &= \text{Re}[I(f_m)] - \{\text{Re}[I(f_{m+1})] + \text{Re}[I(f_{m-1})]\} / 2 \\ \text{Im}[I^*(f_m)] &= \text{Im}[I(f_m)] - \{\text{Im}[I(f_{m+1})] + \text{Im}[I(f_{m-1})]\} / 2. \end{aligned}$$

A specific embodiment of the present invention will be non-limitingly discussed in relation with the appended drawing which shows the amplitude spectrum according to the frequency of an electrochemical system submitted to a sinusoidal excitation of small amplitude and to a voltage step.

It should first be noted that, since the applied voltage is imposed by the analysis tool, the system non-stationarity can only appear as current variations.

The present invention is based on the analysis of the behavior of an electrochemical system submitted to a voltage step. The DFT of the current response mainly translates relaxation phenomena and thus the effect of the system non-stationarity. As shown by the curve in dotted lines on the single drawing, the spectrum of amplitude I of the unit of the current DFT usually exhibits a strong low-frequency response to voltage steps.

Conversely, the response to a sinusoidal excitation of frequency f_m of a stationary system translates as a single line at frequency f_m . In practice, this response corresponds on the one hand to the system response to the excitation at frequency f_m , and on the other hand to the contribution of relaxation effects.

The advantage of the use of the Fourier transform is that the single-frequency spectrum linked to the sinusoidal excitation is superposed to the spectrum linked to the voltage step.

According to the present invention, once the above considerations have been taken into account, it is provided to subtract from the intensity response at frequency f_m the contri-

bution due to relaxations, evaluated based on the analysis of the DFT at frequencies adjacent to f_m . Indeed, the Fourier transform for frequencies f_{m-1} and f_{m+1} of the system will only correspond to non-stationarity phenomena and it will be considered that the amplitude value linked to non-stationarities for a frequency f_m is the average of the values for the two adjacent frequencies.

Thus, the present invention provides:

- setting an electrochemical system to a selected voltage state and applying a single-frequency sinusoidal excitation thereto,

- measuring, without waiting for the system stabilization, the amplitude of the current and of the voltage at regular intervals immediately after application of the voltage while the sinusoidal excitation is applied, and

- calculating, on the one hand, the discrete Fourier transform of the voltage for frequency f_m of the excitation and on the other hand the DFT of the current for value f_m and for two frequencies f_{m-1} and f_{m+1} adjacent to frequency f_m , and

- calculating the value of the complex impedance at frequency f_m based on the value of the TFD of the voltage for frequency f_m and on a corrected value of the TFD of the current, taking into account the TFDs calculated for frequencies f_{m-1} , f_m , and f_{m+1} .

Corrected amplitude I^* of the discrete Fourier transform of the current will be calculated in real value and in imaginary value by the two following equations:

$$\text{Re}[I^*(f_m)] = \text{Re}[I(f_m)] - \{\text{Re}[I(f_{m+1})] + \text{Re}[I(f_{m-1})]\} / 2$$

$$\text{Im}[I^*(f_m)] = \text{Im}[I(f_m)] - \{\text{Im}[I(f_{m+1})] + \text{Im}[I(f_{m-1})]\} / 2.$$

The value of the impedance corrected with the non-stationarity effects then is:

$$Z(f_m) = E(f_m) / I^*(f_m)$$

$$\text{with } I^*(f_m) = \text{Re}[I^*(f_m)] + j \text{Im}[I^*(f_m)]$$

As soon as the reading of the points is performed for frequency f_m , a sinusoidal signal can be applied to a new frequency and a new reading can be performed, and so on.

5 An advantage of the present method is that it makes a
correct impedance analysis on non-stationary electrochemical
systems possible, especially at very low frequencies. At the
same time, a considerable time gain is obtained for systems
which stabilize slowly since with the correction according to
the present invention, it is no longer necessary to wait for the
10 stabilization after powering-on of the system to start an imped-
ance analysis.